A New Fuel Cell Anode Catalyst

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Introduction

The operating cost of a fuel cell power plant is determined primarily by the cost of the fuel. Although hydrogen is generally more expensive than methanol or propane, there are a number of situations in which fuel cells operating on hydrogen could be economical. An example of this is the on-the-site fuel cell oxidation of by-product hydrogen obtained from commercial processes such as the electrolytic production of chlorine. Air would be used as the oxidant.

One of the principal items which affects the capital cost of the fuel cell power plant itself is the cost of the anode and cathode catalysts. The majority of the ambient temperature H_2/O_2 fuel cells described in the literature have employed noble metals such as platinum and palladium. These metals are expensive, and some question has been raised regarding an adequate natural abundance of the elements (1).

There are two alternatives to developing inexpensive catalyst-anodes, either reduce the amounts of the noble metal catalyst on the electrode to about 1 mg/in^2 of electrode, or employ less expensive non-noble metal catalysts.

The latter approach has been followed for example, by E. Justi (2), who successfully constructed hydrogen anodes starting with the Raney alloy (Ni_2Al_3). It would appear, however, that the economic advantage of employing relatively inexpensive metals, nickel and aluminum, is more than balanced by the relatively involved, and hence costly, procedure of electrode preparation. Furthermore, the problems in adapting these procedures to the preparation of large electrodes for the construction of fuel cell power plants may limit the applications of this catalyst.

These problems are not significant with the use of a new, non-noble metal, hydrogen anode catalyst, nickel boride,[3] This material is relatively inexpensive and is easily synthesized in the form of an electrode.

The properties of nickel boride as an anode in the hydrazine/O_2 cell and the KBH_4/O_2 cell have been discussed elsewhere (4,5). It was shown that for these cells, the nickel boride catalyst-anodes were approximately 0.1 volt more effective for the direct fuel cell oxidation of N_2H_4 and KBH_4 than a palladium catalyst.

The chemical hydrogenation properties of this catalyst have been discussed only briefly in the literature. Nickel boride has been reported to be superior in catalyst activity to Raney nickel, and more resistant to fatigue in the hydrogenation of safrole, furfural and benzonitrile (6). Some of the properties of this material have also been described in the Russian literature (7). More recently, H. Brown has discussed the hydrogenation of olefins by nickel boride (8).

Nickel boride can be formed by heating nickel oxide to 700-1000°C in a stream of BCl_3 and H_2 (9). Another method of preparation involves electrolysis of nickel oxide "dissolved in variable quantities of alkali tetraborates" (10). The compound can also be formed directly from the elements by diffusing powdered boron into the reduced nickel (11). However, the most convenient method has been that developed by H. Schlesinger (12) in which Ni_2B is formed by combining solutions of potassium borohydride and a nickel salt.

Chemisorption Porperties

Nickel boride, prepared by the Schlesinger method, is formed in an atmosphere of hydrogen, produced by the decomposition of the excess KBH_4 on the catalyst surface. As a result, there is a considerable quantity of H_2 chemisorbed on the material so that in some cases it may be pyrophoric. However no difficulty was experienced in handling the electrodes.

The chemisorption of hydrogen on nickel boride was studied as a function of temperature. (The sample employed in these experiments had a surface area of 15 m^2/gm, as determined from the physical adsorption of nitrogen at -196°C.) Adsorbed hydrogen was removed by evacuating the sample at 200°C to a pressure of less than one micron. As will be shown below, heating at this temperature has only a minor effect on surface area. The results are summarized in Table I for the adsorption of hydrogen at a pressure of one atmosphere.

TABLE I

Adsorption of H_2 on Ni_2B

Temperature	Volume Adsorbed (STP) (cc/gram)
-196°C	0.6
0°	3.5
25°	3.4
150°	3.2
275°	2.3

The volume of nitrogen required to form a physically adsorbed monolayer on this sample was 3.5 cc/gram. Thus the adsorption of H_2 at room temperature corresponds very closely to a monolayer.

The variation of the quantity of hydrogen adsorbed with temperature, as shown in Table I, is characteristic of activated adsorption. At -196°C, the hydrogen has insufficient energy to overcome the energy barrier for adsorption. At the higher temperatures, (275°) there is sufficient energy to break the chemical bonds holding the hydrogen to the surface of the solid and the quantity of gas adsorbed decreases.

A brief study was also made of the physical structure of the catalyst as a function of sintering temperature. A sample of Ni_2B was heated under vacuum to a range of successively higher temperatures. The surface area of the sample was determined between heat treatments from the N_2 adsorption isotherm.

The sample was first degassed at ambient temperature until a constant pressure of less than one micron was reached. A nitrogen adsorption isotherm, measured at -195°C, indicated a surface area of 22.5 m^2/gm. The boride was then heated under vacuum to 200°C and held at a pressure of less than one micron for four hours. A second nitrogen isotherm indicated a surface area of 21.3 m^2/gm. The decrease is small, indicating little, if any, sintering of the nickel boride. Next, the sample was heated to 350°C for 17-1/2 hours at a pressure of less than one micron. The surface area dropped to 13.3 m^2/gm. Finally the sample was heated to 475°C for 2-1/2 hours. The final surface area was 6.38 m^2/gm. This data is plotted in Figure 1.

Very little chemisorption of hydrogen was noted on the Ni_2B sample after sintering at 350°C. The sample was cooled to 25°C and the hydrogen isotherm measured. After evacuating to a pressure of $<1\mu$ at this temperature to remove only physically adsorbed hydrogen, another hydrogen isotherm was measured. The two isotherms were identical, indicating at most, weakly adsorbed hydrogen. This loss of active adsorption sites on sintering is confirmed by electrochemical data. Fuel cells containing Ni_2B anodes which had been sintered at 500°C did not attain a voltage greater than 0.4V, while the samples sintered at 400°C attained a cell voltage of one volt but only very slowly.

Apparently, the activity of the electrocatalyst was more sensitive to heat treatments than would be expected simply from changes in surface area. A 3" x 3" anode, generating approximately 10 ma/cm^2 must have at least 10^{19} hydrogen atoms chemisorbing and reacting per second. The minimum current involved in the voltmeter reading of 1 volt was approximately 10^{-6} amps, i.e., 10^{13} hydrogen atoms reacting per second. A catalyst-anode sintered at 500°C achieved an open circuit voltage of only 0.4 volt. Assuming a proportionality between the rate of reaction and the number of active sites, there must have been a decrease by a factor of 10^6 in the number of active sites upon sintering at 500°C. The surface area, however, was decreased only by a factor of four.

This conclusion is also apparent from a comparison of the hydrogen chemisorption after sintering at 350°C with the loss of surface area. The chemisorption of H_2 was reduced to a negligable value while the surface area had decreased by a factor of four.

Anode Oxidation of H_2

Nickel boride was studied as a H_2 anode catalyst in two forms, first as the powder and then supported on a porous nickel plaque. The powder was prepared by combining a basic solution of 5% KBH_4 with a dilute aqueous solution of a nickel salt, e.g., nickel acetate. A voluminous black precipitate formed immediately, and was accompanied by a rapid evolution of hydrogen gas. The details of the procedure are all well documented (6) and Ni_2B is the sole, insoluble, reaction product. As a check on the procedure, a sample of this material was analyzed and shown to have a Ni/B atom ratio of 2.05. The plaque-electrode was formed by depositing Ni_2B in the voids of a porous sintered nickel plaque. The substrate, commercially available, measured 3" x 3" x 0.03".

Since the nickel boride is an electrical conductor, it was possible to study the catalyst directly, i.e., it was not necessary to first

support the catalyst on a conducting substrate. The catalyst was formed into a plug and placed in the catalyst test electrode shown in Figure 2. The fuel gas was passed down the metal tube, through the catalyst plug and into the "free" electrolyte. Studying the catalyst in this form alleviated many of the problems involved in operating H_2/O_2 fuel cells, such as maintaining the proper moisture balance in the cell. The two electrodes were "driven" with the commutator (13), hence the voltages measured were IR free. In such a system, H_2 was consumed at the anode and water was electrolyzed at the auxiliary electrode. A saturated calomel electrode, connected to the cell by a salt bridge, was used as the reference electrode. The entire cell was mounted in a constant temperature bath maintained at 80°C. A typical voltage-current curve obtained for a Ni_2B "plug" hydrogen anode is shown in Figure 3. A curve recorded under similar conditions for 1:1 palladium black-graphite mixture is included for comparison purposes. It is apparent that the nickel boride anode is sufficiently active to support high current densities, e.g., 260 ma/cm^2. The palladium-graphite anode is only 0.04 volt more negative than the more economical nickel boride electrode at current densities of 65 to 260 ma/cm^2.

A test electrode was then operated at a constant load of 65 ma/cm^2 and the anode voltage recorded as a function of time. This data is summarized in Figure 4. There is apparently a small fall-off in performance over the first 200 hours, i.e., from -0.87V to -0.83V. The voltage then remained constant for the next 700 hours, at which time the test was terminated. It is quite apparent from this data that Ni_2B is capable of extended performance as a hydrogen anode catalyst.

The Ni_2B catalyst was then evaluated in complete fuel cells of the conventional Allis-Chalmers design, shown in Figure 5. It was possible to apply the active powder directly to the surface of the capillary membrane, and a number of cells of this type were built. Since this procedure is inefficient in the use of catalyst, it was desirable to employ a catalyst support to more efficiently disperse the catalyst across the electrode. As mentioned above, a porous, sintered nickel plaque (3" x 3" x 0.03") was used for this purpose with the Ni_2B catalyst deposited in the pores of the substrate. A voltage-current curve obtained for a fuel cell employing such an anode is shown in Figure 6. The cell temperature in this case was 78°C. It was possible to support a load of approximately 70 ma/cm^2 at a cell voltage of 0.7V. Recent improvements in cell and electrode design have increased this performance to 100 ma/cm^2 @ 0.7V.

Extended Performance Tests

The fuel cell data shown in Figure 6 described the initial performance of the catalyst electrodes, i.e., the voltage-current characteristics obtained during the first day or two of operation. However, fuel cell electrodes generally do show some loss in activity with time as shown in Figure 4. This effect was also studied with a fuel cell of the type shown in Figure 5 employing an anode of Ni_2B deposited onto a porous nickel substrate. The initial performance was essentially that described by the voltage-current curve of Figure 6.

Before discussing the extended performance data, it is necessary to briefly mention the subject of fuel cell "controls". The principal problem, common to all H_2/O_2 fuel cells, centers about maintaining

the proper water balance in the cell. It is desirable to withdraw from the operating fuel cell only that amount of water produced by the fuel cell reaction. If an excess is removed, the cell will dry out; if insufficient water is removed, the electrode will flood and/ or the electrolyte will be diluted. In both cases, the extended performance of the H_2/O_2 fuel cell would be adversely affected.

A high operating current density provides for a high rate of water production and the problem of maintaining the proper amount of water in the cell becomes more severe. The life test on the Ni_2B hydrogen anode was carried out at a relatively low current density, i.e., 32 ma/cm^2. At this level, the rate of water production was determined to be sufficiently low so as not to require an involved water monitoring system. The moisture in the cell was controlled empirically by adjusting the hydrogen flow rate to establishing either a wetting or a dessicating condition as needed. The variation in cell voltage with time is shown in Figure 7 for a cell operated in this manner for 1200 hours. There does appear to be a small, gradual fall-off in cell performance with time. Comparing this data with that of Figure 4, most of the fall-off after the first 200 hours must be ascribed to problems of cell control. Nevertheless, this data is sufficient to establish the point that it is possible to construct large nickel boride catalyst-electrodes which are capable of extended operation as hydrogen anodes.

The data presented was taken with 3" x 3" electrodes. No difficulty has been experienced in adapting the preperative procedures to 6" x 4" nickel boride catalyst-anodes. The use of electrodes of this size in the hydrazine/oxygen fuel cell has already been described (4).

Acknowledgements

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12. Schlesinger, H. I., U.S. Patent 2,461,611 (Jan. 9, 1945).

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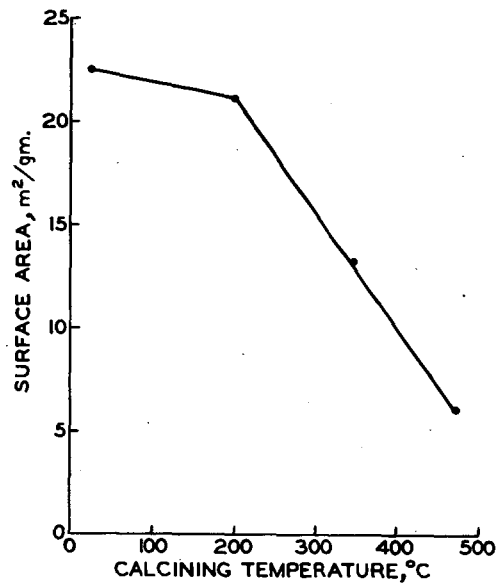Figure 7 - Extended operation of a H_2/O_2 fuel cell employing a nickel boride anode.
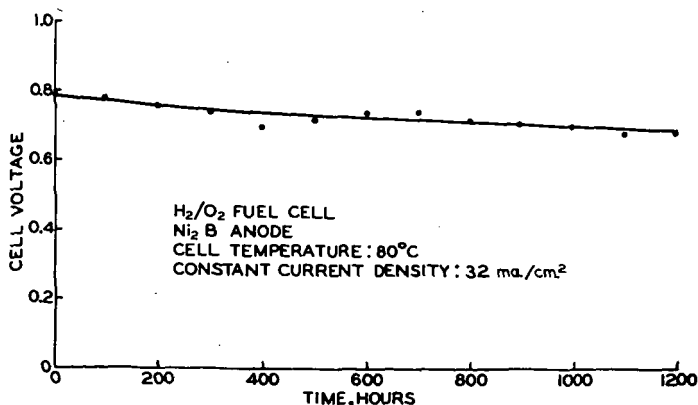
Figure 1 - The variation in surface area with temperature of sintering.
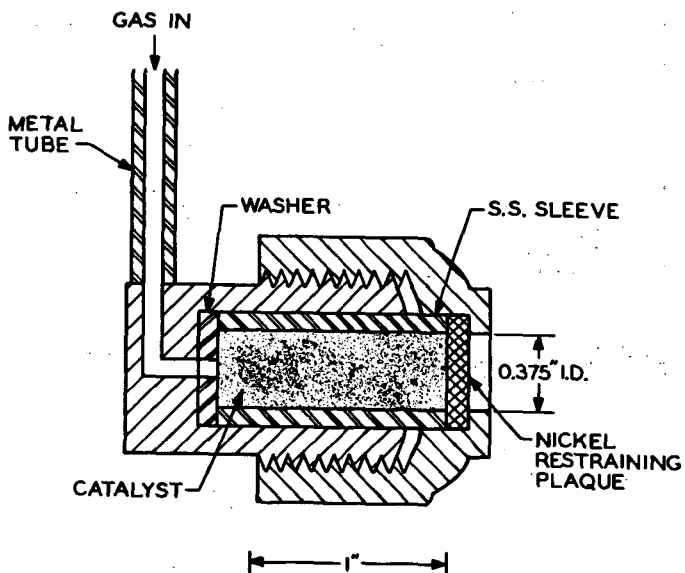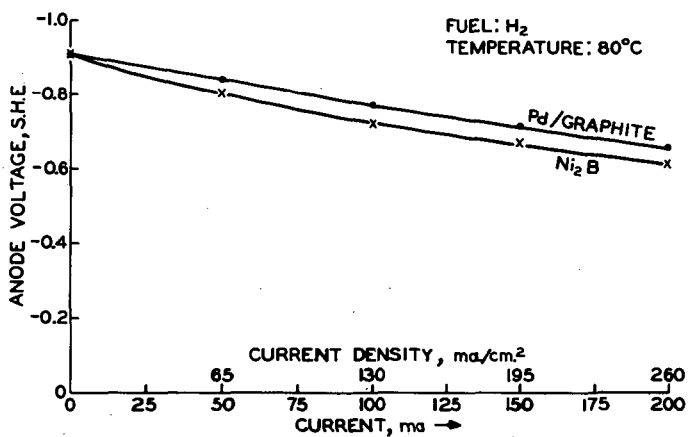

Figure 2 - Catalyst test electrode.

Figure 3 - The anodic oxidation of hydrogen by nickel boride and by palladium black.
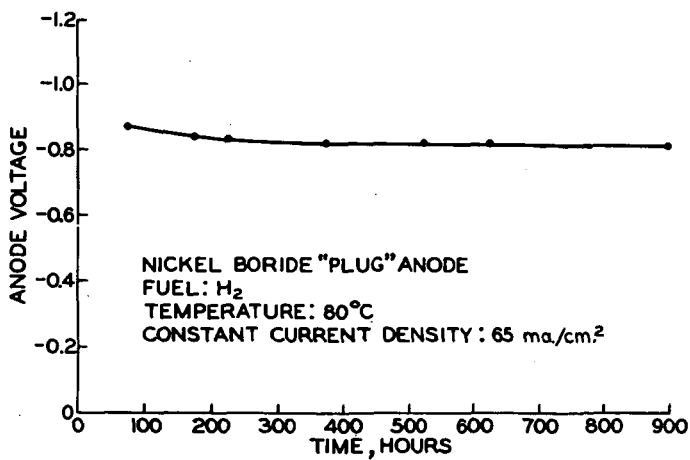

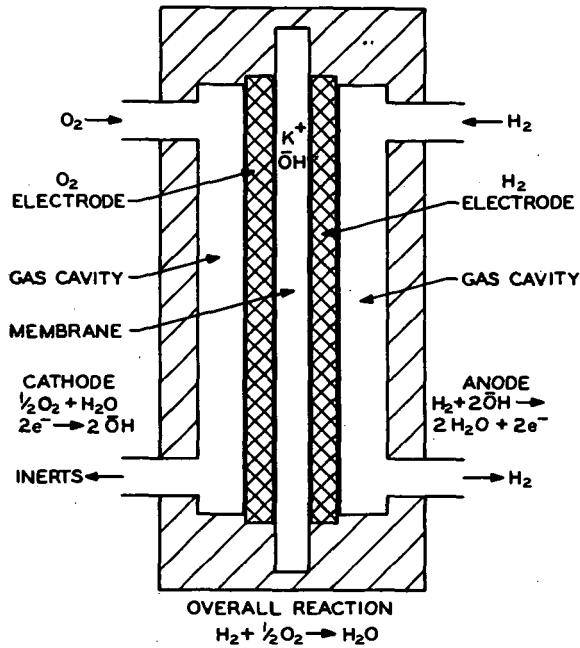Figure 4 - Extended operation of a nickel boride hydrogen electrode.

Figure 5 - Allis-Chalmers H_2/O_2 capillary membrane fuel cell.

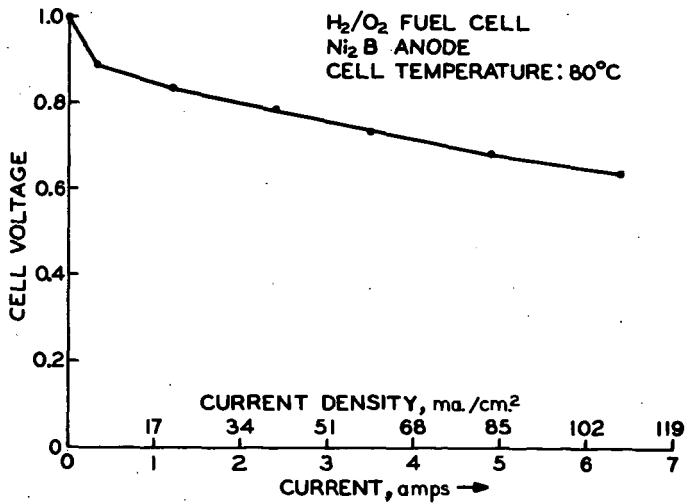Figure 6 - Voltage - Current characteristics of a H_2/O_2 fuel cell employing a Ni_2B anode.